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Influence of various parameters on the a.c. diamagnetic susceptibility of Bi-based superconductors

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Abstract. We present some results of a.c. susceptibility measured on pure and doped with indium and potassium Bi-compounds. For both the 80 K and 110 K phases, we follow the χ' and χ'' variations as a function of (a) the annealing treatment, (b) the Sr/Ca ratio and (c) the doping. Indium doping has either a positive or a negative effect on the 80 K material, depending on the Sr/Ca ratio. It induces an important increase of the superconductive volume of the 110 K material. Effects due to potassium are opposite. The experimental results agree with the fact that T_c goes through a maximum as the hole density increases.

Keywords. Bi superconductors; a.c. susceptibility.

1. Introduction

Extensive studies have been carried out on the new Cu-based superconductor oxides due to their high transition temperature. Nevertheless these materials, in the bulk state, show behaviours which are often very different from the ideal one. Indeed they have a granular, inhomogeneous structure. Materials with not only high transition temperatures but also with narrow ΔT_c are difficult to obtain. However, it is now possible, to make polycrystalline compounds such as Ln $Ba_2Cu_3O_7$ [Ln = rare earth or yttrium] by the classical solid-state reaction with relatively narrow transition. For example, one of the best compounds, $EuBa_2Cu_3O_7$, has a $T_c = 93$ K (midpoint), $\Delta T_c \leqslant 2$ K (magnetic susceptibility), $\Delta T_c \leqslant 1$ K (resistivity) in zero field. But, up to now, such results have not been obtained on bulk Bi-based superconductors. This family includes two groups: the first one, $Bi_2(Sr,Ca)_3Cu_2O_x$ with $T_c \simeq 70$–80 K and the second one, $Bi_2(Sr,Ca)_4Cu_3O_y$ with $T_c \simeq 100$–110 K. The superconductive transitions are either complete but broad or narrow but partial. Indeed, as the condition of preparation of these compounds is very "pointed", they are often inhomogeneous, multi-phased, with small grains; consequently, for this latter reason, they show important effects due to Josephson coupling between the grains.

We have attempted to obtain the best Bi-samples as possible. The a.c. susceptibility measurements allowed us to distinguish between both characteristics: intragrains or intergrains effects (Nicolas and Burger 1990). Usually, the transition temperature T_c is related to the number of holes by CuO_2 plane. We report here some results where this number of holes varies with various parameters such as: oxygen content, Sr/Ca ratio, small doping with cations of different valency.

2. Results

2.1 *80 K compounds*

(i) *Undoped samples*: Two compounds have been studied with a different Sr/Ca ratio: the [4334]-phase with Sr/Ca = 1 and the [2212]-one with Sr/Ca = 2. We have been

able to obtain relatively good samples with a narrow transition compared to the yet known results. For both samples, T_c goes through a maximum as the annealing temperatures increases, but their behaviour is opposite as regards oxygen: for Sr/Ca = 1, T_c is maximum with an additional oxygen whereas for Sr/Ca = 2, a release of oxygen is necessary to reach a T_c maximum. The variations of χ' and χ'' with the a.c. field show that the grains remain small compared to the near T_c penetration depth.
(ii) *Doped samples*: The trivalent In and the monovalent K^+ have been checked. In the case of In^{+++}-doping, T_c decreases a little and the superconductive volume diminishes quickly when Sr/Ca = 1 whereas the effect is opposite with respect to T_c in the case of Sr/Ca = 2. Indeed T_c increases, goes through a maximum and decreases with In-concentration. The superconductive volume does not vary and remains maximum for the studied concentrations ($0 \leqslant x \leqslant 0{\cdot}3$) (Nicolas *et al* 1990). Doping with potassium induces opposite effects on the [2212] phase.

All these results can be well understood if one considers that, as shown previously for $La_{2-x}Sr_xCuO_4$ (Torrance *et al* 1988) and for $Bi_2(Sr, Ca)_3Cu_2O_{8\pm\delta}$ (Buckley *et al* 1988; Koike *et al* 1989), the variations of T_c as a function of p, the hole density, presents a maximum. In the case of the Bi-compound, the density of holes would be governed by the Sr/Ca ratio. When Sr/Ca = 1, p is such that T_c is not at the maximum value (before the maximum) and it is necessary to oxidize a little to reach T_c maximum whereas for Sr/Ca = 2, p is such that T_c is situated after the maximum and it is necessary to deoxidize in order to reach T_{max}As In^{+++} decreases the density of holes if substituted the Ca^{++} and K^+ increases it if substituted to Bi^{+++}, the above mentioned opposite behaviours can be well explained.

2.2 *110 K compound*

It corresponds to an additional $CaCuO_2$ plane in the structure of $Bi_2Sr_2CaCu_2O_8$. Its formula would be $Bi_2(SrCu)_4Cu_3O_{10}$. The monophased system is very difficult to obtain. In-doping decreases T_c slightly (110 K–106 K) but increases strongly the superconductive volume. K-doping provokes an opposite behaviour.

3. Conclusion

We have been able to prepare nearly-pure Bi-phases. The χ' and χ'' measurements allow us to determine various factors such as homogeneity, grain size, coupling between grains etc. Our most important result is the significant increase of the 110 K-phase volume by In-doping.

References

Buckley R G 1988 *Physica* **C156** 629
Koike Y *et al* 1989 *Physica* **C159** 105
Nicolas M and Burger J P 1990 (to be published)
Nicolas M, Burger J P and Negri J 1990 (to be published)
Torrance J B *et al* 1988 *Phys. Rev. Lett.* **61** 1127